UNIVERSITY OF TORONTO
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Dushman, Saul
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THESIS

SUBMITTED

TO THE SENATE OF THE UNIVERSITY OF TORONTO

IN ACCORDANCE WITH THE REQUIREMENTS

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

SAUL DUSHMAN

The Behavior of Copper Anodes in Chloride Solutions

Reprinted from
e Journal of Physical Chemistry. Vol. XIV.

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The Registrar,
University of Toronto,

Sir:

I beg to recommend that the thesis entitled "The behavior of copper anodes in chloride solutions", submitted by Mr. Saul Dushman, be accepted for the degree of Doctor of Philosophy.

I am, Sir,
Yours truly,

(Signed) W. LASH MILLER,
Professor of Physical Chemistry.

The Chemical Laboratory,
April, 1910.

I hereby certify that the thesis above mentioned has been accepted by the Senate of the University of Toronto for the Degree of Doctor of Philosophy, in accordance with the terms of the Statute on that behalf.

(Signed) JAMES BREBNER,
Registrar.

The University of Toronto.
March 23rd, 1911.

THE BEHAVIOR OF COPPER ANODES IN CHLORIDE SOLUTIONS

BY SAUL DUSHMAN

INTRODUCTION

In connection with some experiments on the electrolytic etching of copper alloys, my attention was drawn to the behavior of pure copper anodes in solutions of chlorides. I found that it was possible to make the copper dissolve wholly as cupric or wholly as cuprous salt or as a mixture of these in any desired proportions, by varying the current density or the concentration of chloride in solution. The observation that increasing the concentration of chloride increases the proportion of cuprous salt formed,[1] suggested that there may be equilibrium at the surface of the electrode between metallic copper and the cuprous and cupric salts in solution. The effect on the proportion of cuprous salt consequent on lowering the current density,[2] stirring the solution,[3] or increasing the rate of circulation,[4] may also be explained in the same manner; for all these processes tend to lessen the difference in composition between the solution at the electrode and that in the body of the electrolyte, *i. e.*, they raise the concentration of the chloride and diminish that of the dissolved copper salts at the surface of the anode,[5] and thus increase the proportion of cuprous salt formed.[6]

The assumption of equilibrium at the electrode is not new,[7] it has been put forward to explain the behavior of gold anodes

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[1] See experiments 1–6 Table I.

[2] See experiments 10–12 Table II.

[3] Compare experiments 7 and 8 5 and 9 Table I.

[4] See experiments 13–16 Table II.

[5] See abstract of preliminary work, Trans. Roy. Soc. Can. Sec. III, p. 26 (1907).

[6] A brief account of these experiments was given at the meeting of the American Chemical Society at Toronto, June 1907.

[7] Foerster: Elektrochemie wässr. Lösungen, p. 212, etc.

TABLE I

Beaker experiments. Stationary electrodes. Hydrochloric acid solutions. Area of electrodes = 2.5 × 2.5 cms

No.	Concentration	Current density (Amps/cm^2) gram	Total copper dissolved gram	Percent cupric	Percent cuprous	Stirring
1	N/1	0.02286	0.760	0	100	Yes
2	N/10	0.02286	0.429	87	13	Yes
3	N/40	0.02286	0.341	100	0	Yes
4	N/1	0.00514	0.602	0	100	Yes
5	N/2	0.00514	0.508	30	70	Yes
6	N/4	0.00514	0.372	77	23	Yes
7	N/1	0.00416	0.609	0	100	Yes
8	N/1	0.00416	0.422	53	47	No
9	N/2	0.00514	0.360	80	20	No

TABLE II

Beaker experiments. Circulating electrolyte. Rotating anode. Solution N/10 HCl. Duration of each experiment, 30 minutes

	Volume circulated liters	Current density (Amp./cm^2)	Total copper dissolved	Percent cupric	Percent cuprous
10	10.6	0.016	0.2392	16.0	84.0
11	11.0	0.107	0.9403	94.0	6.0
12	10.0	0.300	2.7000	100.0	0.0
13	15.7	0.109	1.0107	88.2	11.8
14	33.5	0.109	1.0523	83.7	16.3
15	39.0	0.109	1.0910	79.3	20.7
16	48.4	0.109	1.1354	74.4	25.6

in chloride solutions[1] of copper anodes in sulphate solutions[2] and of anodes of tin, antimony and bismuth in a number of different electrolytes.[3] *In no case however have quantitative measurements been made by which the hypothesis of equilib-*

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[1] Wohlwill: Zeit. Elektrochemie, **4**, 405 (1898).

[2] Foerster and Seidel: Zeit. anorg. Chem., **14**, 106 (1897).

[3] K. Elbs and H. Thummel: Zeit. Elektrochemie, **10**, 364 (1904); K. Elbs and J. Forssell: Ibid., **8**, 760 (1902); K. Elbs: Ibid., **8**, 512 (1902); K. Elbs and F. Fischer: Ibid., **7**, 343 (1900).

rium could be controlled, and the object of the experiments described in this paper is to supply this deficiency.[1]

My electrolyses were consequently carried out under conditions that allowed the concentrations of the various constituents of the solution at the anode to be ascertained; and the concentrations so determined were compared with the requirements of the Mass Law.

APPARATUS

In designing the apparatus it was necessary first to provide a uniform field, so that the current density might be the same at every part of the anode, second, to exclude air as far as possible, so that there might be no "chemical" solution of the anode, and third, to keep the copper salts from reaching the cathode, so that the composition of the electrolyte might depend only on the anode reactions. Arrangements had also to be made for varying the composition and rate of circulation of the electrolyte, as well as the rate of rotation of the anode. The current was determined by an ammeter and a copper (or silver) voltameter in the circuit.

Fig. 1. shows the apparatus finally used.[2] It consisted of two porous cylinders P_1 and P_2 cemented to the cylinder E and the bottom piece F which were of hard rubber, and a rotating copper anode A making contact by means of a wire W with a shaft S and holder H. A plug of hard rubber T was provided with a threaded perforation so that it could be tightened against the copper tube as shown in the diagram. The tube could therefore be taken off the shaft and weighed. Rubber rings *r* and pieces of tubing *b* prevented any electrolyte entering the tube. The access of air to the solution passing over the anode was prevented by means of hydrochloric acid (of the same strength as that circulating through the cell) which was contained in the circular groove R in which rotated the hard rubber cover C. The electrolyte entering B passed over the anode, through the glass tube K

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[1] NOTE.—After these experiments were well under way, an abstract of a paper originally published in Russian appeared in Chem. Cent. 2, 1243 (1907) in which the hypothesis is advanced that equilibrium exists at the surface of copper anodes in chloride solutions and of mercury anodes in nitrate solution. No quantitative measurements however are given except in the case of mercury in solution of potassium nitrate.

[2] A description of an earlier form of apparatus will be found in Trans. Am. Electrochem. Soc., 13, 314 (1908).

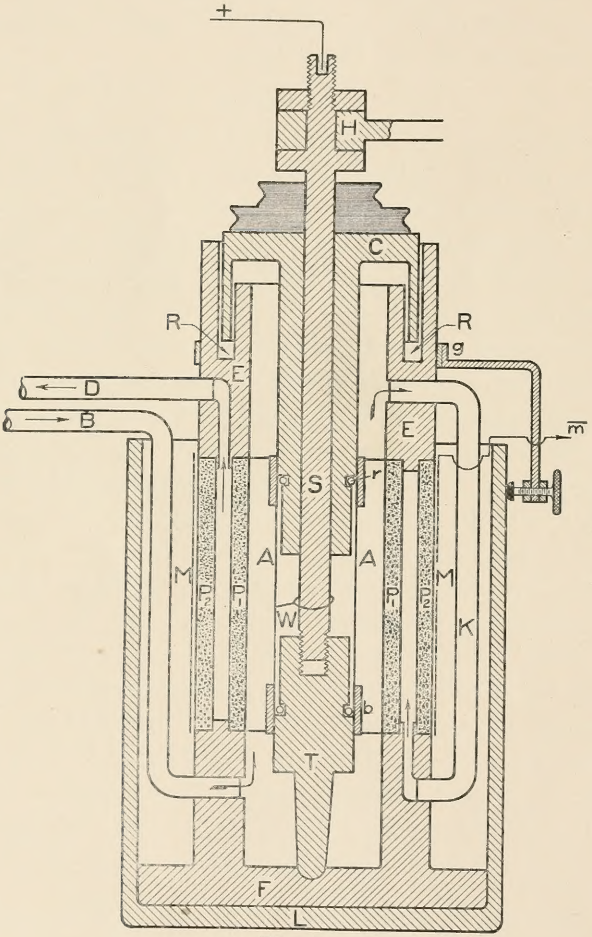

Fig. 1

into the compartment between the two porous cylinders and left it by means of the exit tube D. The cathode consisted of a platinum gauze M wrapped around the outside of P. The different parts of the apparatus were cemented together with a cement consisting of one part rubber and three parts resin. Three rubber-tipped screw clamps *k* attached to a brass ring g and clamped to the glass jar L (which contained the cathode solution) prevented any lateral motion of the cell when the anode was set rotating.

The stock solution, contained in a tubular 12-liter bottle, was freed from air by exhaustion (a mercury manometer was used to indicate the degree of exhaustion), and was then saturated with purified carbon dioxide gas. During the electrolysis, this solution was kept under an atmosphere of the gas and furthermore on its way from the tubulus into the inlet tube B of the cell it was joined by a stream of carbon dioxide gas; in this manner the cell could be filled with the gas before electrolysis, and oxidation of cuprous salt formed during the experiment was reduced to a minimum. After circulating through the cell once, the electrolyte passed into a measuring cylinder and was then discarded.

With these precautions to exclude air, the loss of weight of the anode when rotated (without current) was extremely small as is evident from the following data:

Hydrochloric acid (1.84×10^{-2} N) was circulated through the cell for one hour. In the first two experiments air-saturated solution was used, in the third, solution which had been completely freed from air by exhaustion and saturated with carbon dioxide gas, and in the fourth, a mixture of equal volumes of air-saturated and carbonated solutions.

No.	V	L	$10^3 L/V$
1	3.2	0.0148	4.6
2	2.4	0.0085	3.5
3	2.7	0.0008	0.3
4	2.2	0.0050	2.3

Under V is given the number of liters of solution circulated, and under L, the loss in weight of the copper tube. It appears from these results that the rate of solution of the copper in hydrochloric acid solutions containing air is approximately proportional to the concentration of oxygen.

In another experiment with 5×10^{-3} N acid, 6.0 liters solution (air-free) were circulated in an interval of 7 hours and only 0.0028 gram was dissolved,[1] corresponding to 0.45×10^{-3} gram per liter.

THE CONCENTRATIONS IN THE BODY OF THE SOLUTION

To find the quantity of cupric and cuprous salts, respectively, formed during an experiment, the total copper dissolved in an experiment (P grams) was compared with the copper (Q) or silver, deposited in a voltameter in the circuit. Then 2(P-Q) gms is the weight of copper dissolved as cuprous salt, and 2Q-P is the weight of copper as cupric.

The concentrations of the cupric and cuprous salts in the electrolyte, expressed in *mols per litre*,[2] may therefore be represented by

$$[\text{Cupric}] = \frac{2Q - P}{63.6\,V}$$

$$[\text{Cuprous}] = \frac{2(P - Q)}{63.6\,V},$$

where V is the total volume of the electrolyte passed through the cell (in liters).[3] In the calculations which follow, it is assumed that the cupric salt is totally dissociated in solution into the ions $\overset{++}{\text{Cu}}$ and $\overset{-}{\text{Cl}}$, so that

$$[\overset{++}{\text{Cu}}] = \frac{2Q - P}{63.6\,V}. \qquad \text{(I)}$$

The cuprous salt on the other hand is assumed to exist in two forms,[4] $\overset{+}{\text{Cu}}$ and $\overset{-}{\text{CuCl}_2}$, so that

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[1] As the anode itself weighed about 75 g. these small losses could not be determined with accuracy.

[2] By one mol cuprous or cupric salt is understood the quantity containing 63.6 g. copper. The concentrations in the body of the solution are distinguished by square brackets.

[3] This assumes that the solution passing through the cell arrives at a stationary composition in an interval of time which is very small compared to the total duration of the experiment.

[4] Bodländer and Storbeck: Zeit. anorg. Chem., 31, 1 (1902). In a paper which will be published shortly, these equilibrium experiments will be discussed more fully.

$$[\overset{+}{\mathrm{Cu}}] + [\mathrm{Cu}\overset{-}{\mathrm{Cl}}_2] = \frac{2(\mathrm{P} - \mathrm{Q})}{63.6\ \mathrm{V}}. \qquad \text{(II)}$$

It was thought by Bodländer and Storbeck that the ratio $\overset{+}{\mathrm{Cu}}/\mathrm{Cu}\overset{-}{\mathrm{Cl}}_2$ would be given by

$$(\overset{+}{\mathrm{Cu}}) \times (\overset{-}{\mathrm{Cl}})^2 \Rightarrow \mathrm{K}' (\mathrm{Cu}\overset{-}{\mathrm{Cl}}_2) \qquad \text{(III)}$$

corresponding to the chemical equation

$$\overset{+}{\mathrm{Cu}} + 2\overset{-}{\mathrm{Cl}} \rightleftarrows \mathrm{Cu}\overset{-}{\mathrm{Cl}}_2.$$

Careful examination of their results, and some work of my own, however, shows that the "constant," K′, varies from 1.22×10^4 to 6.13×10^4 in different experiments. I have consequently thought it best to plot

$$y = \frac{(\overset{+}{\mathrm{Cu}})}{(\overset{+}{\mathrm{Cu}}) + (\mathrm{Cu}\overset{-}{\mathrm{Cl}}_2)}$$

from their experiments (Table III) with different values of $(\overset{-}{\mathrm{Cl}})$ and to use the graph (Fig. 2) instead of equation (III).

Table III

Solubility determinations of cuprous chloride in potassium chloride solutions (Bodländer and Storbeck)

$\overset{-}{\mathrm{Cl}}$	$(\overset{+}{\mathrm{Cu}})$	$(\overset{+}{\mathrm{Cu}}) + (\mathrm{Cu}\overset{-}{\mathrm{Cl}}_2)$	y
4.55	0.398	0.646	0.616
4.38	0.246	0.484	(0.508)[1]
4.65	0.336	0.589	0.570
5.03	0.263	0.534	0.492
5.28	0.178	0.460	0.387
6.37	0.175	0.514	0.340
9.97	0.233	0.761	0.306
13.76	0.282	1.022	0.276
17.80	0.205	1.122	0.183

(N. B. All the concentrations in this table are expressed in millimols per liter.)

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[1] This determination was not used in plotting the curve. In the graph (see p. 906) the "chlorion" is in the same units as those used in the above table.

THE CONCENTRATIONS AT THE ELECTRODE

Immediately at the surface of the anode, the concentrations of the copper salts are greater than those in the body of the solution, the difference depending on the rate at which the copper is being dissolved. If it be assumed that the copper salt formed must diffuse through an adherent liquid film of constant thickness, l cms., and that the "diffusion-constant," k (in $\mathrm{cm}^2/\mathrm{sec.}$) is independent of the concentration, then the difference in concentration due to the diffusion is given by

$$\frac{10^3 l}{k} \times \frac{\text{(Mols salt formed per second)}}{\text{(Area of electrode in cms}^2\text{)}}.$$ [1]

These assumptions may be made in the case of the copper salts and hydrochloric acid, so that if the concentrations at the anode be distinguished from those in the body of the solution by the use of curved brackets, { },

$$\{\overset{+}{\mathrm{Cu}}\} + \{\overline{\mathrm{CuCl}_2}\} = \frac{2(\mathrm{P} - \mathrm{Q})}{63.6}\left(\frac{1}{\mathrm{V}} + \frac{10^3 l}{k_1 \mathrm{A}\, t}\right) \qquad \text{(IV)}$$

$$\{\overset{++}{\mathrm{Cu}}\} = \frac{(2\mathrm{Q} - \mathrm{P})}{63.6}\left(\frac{1}{\mathrm{V}} + \frac{10^3 l}{k_2 \mathrm{A}\, t}\right) \qquad \text{(V)}$$

where k_1 is the diffusion-constant of cuprous salt, k_2 that of cupric, A, the area of the electrode-surface (in cms^2) and t, the duration of the electrolysis in seconds.

Values of $\{\overline{\mathrm{Cl}}\}$, the concentration of chlor ion at the electrode, may be calculated from the equation,

$$\frac{4(\mathrm{P} - \mathrm{Q})(1 - y)}{63.6\, t} = \frac{k_3 \mathrm{A}}{10^3 l}\left([\overline{\mathrm{Cl}}] - \{\overline{\mathrm{Cl}}\}\right) + \frac{\mathrm{HQ}}{31.8\, t}, \qquad \text{(VI)}^2$$

where the term on the left denotes twice the number of mols $\overline{\mathrm{CuCl}_2}$ formed per second at the electrode; the first term on the right, the number of mols $\overline{\mathrm{Cl}}$ reaching the anode per second by diffusion; and the last term, the number of mols

---

[1] Since k, l, and the area of the electrode are measured in cm-units, the factor 10^3 is necessary to convert the concentration difference into *mols per liter.*

[2] k_3 is the diffusion constant of hydrochloric acid and H, the transport number of chlorine in the solution.

$\overline{\mathrm{Cl}}$ transported electrolytically to the anode per second. Thus,

$$\{\overline{\mathrm{Cl}}\} = [\overline{\mathrm{Cl}}] - \frac{10^3 l[2(\mathrm{P}-\mathrm{Q})(1-y)-\mathrm{HQ}]}{31.8\,k_3\mathrm{A}t}. \qquad \text{(VII)}$$

As in my experiments $\{\overline{\mathrm{Cl}}\}$ and $[\overline{\mathrm{Cl}}]$ do not differ greatly, an approximate value of

$$y = \frac{[\overset{+}{\mathrm{Cu}}]}{[\overset{+}{\mathrm{Cu}}] + [\overline{\mathrm{CuCl}}_2]}$$

calculated on the assumption that $\{\overline{\mathrm{Cl}}\}$ and $[\overline{\mathrm{Cl}}]$ are equal, is sufficiently accurate for the purpose of equation (VII).

Using the value of $\{\overline{\mathrm{Cl}}\}$ calculated according to this equation, the ratio,

$$Y = \frac{\{\overset{+}{\mathrm{Cu}}\}}{\{\overset{+}{\mathrm{Cu}}\} + \{\overline{\mathrm{CuCl}}_2\}} \qquad \text{(VIII)}$$

was determined from the graph.

APPLICATION OF THE MASS LAW

Eliminating $\{\overset{+}{\mathrm{Cu}}\} + \{\overline{\mathrm{CuCl}}_2\}$ from (IV) and (VIII), and comparing the result with (V), there follows,

$$\frac{\{\overset{++}{\mathrm{Cu}}\}}{\{\overset{+}{\mathrm{Cu}}\}^2} = \frac{\dfrac{(2\mathrm{Q}-\mathrm{P})}{63.6}\left(\dfrac{1}{\mathrm{V}} + \dfrac{10^3 l}{k_2\mathrm{A}\,t}\right)}{\left(\dfrac{2Y(\mathrm{P}-\mathrm{Q})}{63.6}\left(\dfrac{1}{\mathrm{V}} + \dfrac{10^3 l}{k_1\mathrm{A}\,t}\right)\right)^2}. \qquad \text{(IX)}$$

According to the Mass Law applied to the reaction,

$$\overset{\circ}{\mathrm{Cu}} + \overset{++}{\mathrm{Cu}} \rightleftarrows 2\overset{+}{\mathrm{Cu}}$$

the expression (IX), in which nothing but experimentally determinable quantities appear, ought to be a constant. In the tables which follow I have denoted it by K.

Of the quantities involved in (IX), Q, P, V, A, *t*, and *Y* have already been discussed; there remain only the two ratios l/k_1 and l/k_2. These were determined directly as described in the following sections; in order to check the results, l itself was determined (page 899) and the resulting values of k_1 and k_2, were compared with those deducible from theoretical considerations.

In calculating Y, two other constants were employed, *viz.*, H and k_3. Of these H = 0.167 is taken from the recent measurements of Noyes and Kato,[1] which are in accord with those of Jahn.[2] The diffusion constant of hydrochloric acid, $k_3 = 2.67 \times 10^{-5}$ is obtained from the work of Öholm[3] by averaging his results from 0.01 and 0.02 normal acid and converting into the units (cm^2/sec.) of the present paper.

Determination of l/k_2

The following method for the determination of this constant suggested itself during the course of the investigation.

Solutions containing hydrochloric acid and copper chloride in known quantities were passed through the cell of the apparatus shown in Fig. 1, while the copper cylinder A was revolving without current. The loss in weight (W grams) of the copper was determined while V liters of the solution passed through the cell in the interval t seconds.

Under these circumstances the cupric chloride at the immediate surface of the copper is reduced almost quantitatively to cuprous salt.[4] Assuming that the rate of reduction of the cupric chloride is very much greater than the rate at which it is renewed by diffusion,[5] it follows that the concentration of cupric chloride at the immediate surface of the copper must be practically zero, and consequently that the rate of flow of cupric chloride through the diffusion-film is equal to its rate of reduction. That is,

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[1] A. A. Noyes and Y. Kato: Zeit. phys. Chem., **62**, 420 (1908).

[2] H. Jahn: Zeit. phys. Chem., **58**, 641 (1907).

[3] L. W. Öholm: Zeit. phys. Chem., **50**, 309 (1904).

[4] Bodländer and Storbeck: Zeit. anorg. Chem., **31**, 1 (1902).

[5] Bodländer and Storbeck's experiments: loc. cit. show that the reduction is very rapid.

$$\frac{\mathrm{W}}{63.6\,t} = \frac{k_2\mathrm{A}}{10^3 l}[\overset{++}{\mathrm{Cu}}] \qquad \text{(X)}$$

where $[\overset{++}{\mathrm{Cu}}]$ denotes the concentration of cupric chloride in the body of the solution (in mols per liter). The following table gives the experimental data, together with the values of l/k_2 calculated by means of (X).

TABLE IV[1]

Temp. = 18°, A = 47, rate of rotation = 1600 per minute

No.	[HCl]	$[\overset{++}{\mathrm{Cu}}]$	W	t	V	l/k_2
1	0.0930	0.0497	0.2220	3600	2.2	2350
2	0.0920	0.0484	0.3496	5400	3.5	2220
3	0.0964	0.0072	0.1497	3600	3.1	500
4	0.0966	0.0059	0.1697	4800	3.4	495
5	0.0933	0.0035	0.1565	5400	3.25	360

These measurements show that while l/k_2 increases very rapidly with the dilution in concentrated solution, it tends to attain a constant value for extremely dilute solutions. As the concentrations of cupric chloride obtained in the electrolytic experiments were all less that used in experiment 5 of the above table, the assumption may be made that l/k_2 is constant for these concentrations, and for reasons which will be discussed subsequently (in the section on diffusion constants) the value $l/k_2 = 333$ has been used in the calculations which follow.

Determination of l/k_1

The solubility experiments described in the previous section were also used for the determination of l/k_1. Assuming that at the immediate surface of the copper the solution is saturated with cuprous chloride, values of {*Total Cuprous*} may be calculated from the solubility measurements of Bodländer and Storbeck[1] and inserted in the equation,

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[1] In experiments 3, 4, and 5, the quantity of cupric salt reduced to cuprous has been allowed for when calculating $[\overset{++}{\mathrm{Cu}}]$.

$$\frac{W}{63.6\,t} = \tfrac{1}{2} \times \frac{k_1 A}{10^3 l}(\{\text{Total Cuprous}\} - [\text{Total Cuprous}]), \qquad \text{(XI)}$$

whence values of l/k_1 may be calculated. In this equation the expressions in curved brackets { } and square brackets [ ] denote concentrations (in mols per liter) at the electrode and in the solution respectively, and W, *t*, and A have the same values as in Table IV. The values of [*Total Cuprous*] have been calculated by the relation,

$$[\text{Total Cuprous}] = \frac{2\,W}{63.6\,V}. \qquad \text{(XII)}$$

TABLE V

No.	{Total Chlorine}	{Total Cuprous}	[Total Cuprous]	l/k_1
1	0.1890	0.00850	0.00318	(125.0)
2	0.1890	0.00850	0.00313	122.6
3	0.1107	0.00500	0.00152	125.0
4	0.1099	0.00495	0.00157	142.9
5	0.1028	0.00463	0.00152	160.4
			Average =	138.0

In the subsequent calculations of this paper, the value, $l/k_1 = 138$ has consequently been used.

While the values of l/k_1 and of l/k_2 determined in the above manner give sufficient information for the purpose of equation (IX), it nevertheless seemed desirable to obtain independent values of l, k_1 and k_2, so that the latter might be compared with the values deducible from the mobilities by means of Nernst's formula. These determinations, which

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[1] Loc. cit. For the concentrations of chlorine used in these solubility experiments,

$$\{\text{Total Cuprous}\} = \frac{\{\text{Total Chlorine}\}}{22.2}$$

are detailed in the following paragraphs resulted in the adoption of a valve of l/k_2 slightly lower than the lowest found in Table IV.

Determination of *l* the Thickness of the Film

A. From Experiments with Oxalic Acid

Ackerberg,[1] using a platinized platinum anode, found that the rate of oxidation of oxalic acid dissolved in large excess of sulphuric acid (20 percent conc. H_2SO_4 by volume), may be represented by the equation.

$$\frac{dx}{dt} = \frac{k(B - x)}{V}, \qquad \text{(XIII)}$$

when high current densities are used and the electrolyte is stirred. In this equation, dx/dt gives the number of equivalents oxalic acid oxidized per second and B is the number of equivalents oxalic acid in V liters of the solution at $t = 0$.

Nernst and Brunner[2] and Lorenz[3] have shown that this result is in accord with the hypothesis of diffusion towards the electrode, according to which the number of equivalents oxidized per second is equal to that diffusing to the electrode in the same time. That is, for current densities greater than the limiting value, k (in equation XIII) $= k_4\ A/10^3 l$, where k_4 is the diffusion constant of oxalic acid (in cm²/sec.), A, the area of the electrode (in cms²) and l the thickness of the film (in cms).

Making this substitution in (XIII) and integrating, we find.

$$\frac{k_4 A}{10^3 l V} = \frac{2.3}{t_2 - t_1}\left(\log_{10}\frac{B - x_1}{V} - \log_{10}\frac{B - x_2}{V}\right), \qquad \text{(XIII}a\text{)}$$

where x_1 and x_2 are the number of equivalents oxalic acid oxidized at the end of intervals t_1 and t_2 respectively.

From a knowledge of k_4, A, and the rate of oxidation of a solution of oxalic acid in maximum conductivity sulphuric acid, it is therefore possible to determine l. The value of

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[1] Ackerberg: Zeit. anorg. Chem., **31**, 161 (1902).

[2] Zeit. phys. Chem., **47**, 52, 56 (1904).

[3] Electrochemie, **1905**, pp. 239–44.

k_4 was calculated from the mobility of $\overset{--}{C_2O_4}$ by applying Nernst's equation[1] as modified by Abegg and Bose,[2]

$$k_4 = \frac{u}{2} \times \frac{0.04485}{86400}. \qquad \text{(XIV)}$$

Since $u = 39$ for decinormal oxalic acid, therefore $k_4 = 1.01 \times 10^{-5}$.

In order to obtain a value for l under conditions as nearly similar as possible to those obtaining in the electrolytic experiments with hydrochloric acid solution, the same shaft and stirring arrangement were used as that described on page 888. The copper tube, however, was covered with platinum foil and platinized according to the directions of Kohlrausch and Holborn,[3] and the cell of Fig. 1 was replaced by a porous pot of about 750 cc capacity surrounded by a cylindrical cathode of lead. The electrolyte for the anode compartment contained about 3.5 g crystallized oxalic acid and 200 cc concentrated sulphuric acid per liter, that for the cathode compartment contained the same amount of sulphuric but no oxalic acid.

During the electrolysis, 10 cc samples of the anode solution were pipetted out at definite intervals and titrated against standard permanganate.

TABLE VI

Rate of oxidation of oxalic acid

No.	Current	t	$t_2 - t_1$	$\frac{B-x}{V}$	V	l
—	—	0	—	0.0592	—	—
1	0.45	3600	3600	0.0454	0.63	10.1×10^{-3}
2	0.95	5400	1800	0.0392	0.62	9.3×10^{-3}
3	1.35	6300	900	0.0362	0.61	9.1×10^{-3}
					Average	9.5×10^{-3}

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[1] Nernst: Theoret. Chem., III Auflage, p. 361.

[2] Zeit. phys. Chem., **30**, 545 (1899).

[3] The electrode was platinized while rotating, thus securing a smooth eposit.

B. From Experiments with Copper Sulphate

In the electrolysis of a solution containing both copper sulphate and sulphuric acid, the concentration of the copper at the immediate surface of the cathode is lowered as the current density is increased until a value of the latter is attained at which the concentration is practically zero. Increasing the current density still more causes hydrogen to be liberated along with the copper, which is indicated by an abrupt rise in voltage over the cell.

Just before this point is reached the amount of copper removed from the electrolyte is equal to that carried to the electrode by diffusion, since in the presence of sulphuric acid migration of the copper may be neglected. Thus,

$$\frac{I' \times 31.8}{96540} = \frac{k_5 A}{10^3 l}[CuSO_4], \qquad (XV)$$

where I′/A is the current density at which hydrogen first appears, k_5 is the diffusion constant (in cm²/sec.) of copper sulphate and the expression in square brackets denotes concentration in grams per liter.

Working with the apparatus described on p. 888 (where A = 47) I found $I' = 0.069$ at 18° C and 1600 revolutions per minute (see Tables VII and VIII). The diffusion constant of copper sulphate is given by Wiedeburg[1] as $0.4479 \times 10^{-5} \times (1 - 3.467c)$ where c denotes the concentration in grams of copper per cm³. Sand[2] found the same value for solutions of copper sulphate in sulphuric acid (0.0881 to 0.1804 normal). For the concentration of copper used in the experiments recorded in Tables VII and VIII $k_5 = 0.44 \times 10^{-5}$. Hence using $I' = 0.069$, $l = 4 \times 10^{-3}$.

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[1] Wied. Ann., **41**, 675 (1890).

[2] Phil. Mag. [6], **1**, 45 (1901).

TABLE VII

Determination of limiting current

Experiment I		Experiment II	
Voltage	Current	Voltage	Current
0.125	0.021	0.125	0.020
0.160	0.025	0.160	0.026
0.200	0.035	0.190	0.030
0.280	0.057	0.240	0.040
0.300	0.067	0.320	0.067
0.340	0.110	0.380	0.120
—	I′ = 0.067	—	I′ = 0.068

TABLE VIII

Determination of limiting current

While these readings were taken, the electrolyte was allowed to flow over the cathode as in the experiments of Tables X and XI.

Experiment III		Experiment IV	
Voltage	Current	Voltage	Current
0.17	0.022	0.18	0.020
0.20	0.030	0.20	0.025
0.25	0.040	0.26	0.033
0.34	0.065	0.32	0.050
0.38	0.110	0.37	0.067
0.40	0.115	0.42	0.110
0.40	0.122	0.48	0.140
—	I′ = 0.070	—	I′ = 0.070

The value of l obtained by the oxalic method is higher than that obtained by the second. This is probably due to the value selected for the diffusion-constant of oxalic acid. The diffusion constant for copper calculated from the mobility (at the concentration used in the above experiments) is 0.7×10^{-5} while the direct experiments quoted above gave 0.44×10^{-5}. If the calculated value of the diffusion constant of oxalic acid be reduced in the same proportion, l as calculated by the first method becomes 6×10^{-3}.

Diffusion Constants of Cupric and Cuprous Chlorides

Although the diffusion constant for copper sulphate has been determined for concentrated aqueous solutions and for solutions containing sulphuric acid (see above p. 899) there are no data for the diffusion constant of copper in very dilute solutions of cupric chloride containing hydrochloric acid. From the values of l/k_2 in Table IV and the result $l = 4 \times 10^{-3}$, the following numbers are calculated for k_2.

TABLE IX

No	$\{\overset{++}{\mathrm{Cu}}\}$	k_2
1	0.0479	0.17×10^{-5}
2	0.0485	0.18×10^{-5}
3	0.0072	0.80×10^{-5}
4	0.0059	0.81×10^{-5}
5	0.0035	1.11×10^{-5}

These numbers show that k_2 increases with the dilution. Using the value 50.5 for the mobility of $\overset{++}{\mathrm{Cu}}$ at infinite dilution,[1] k_2 may be calculated from the equation

$$k_2 = \frac{u}{2} \times \frac{0.04485}{86400} \qquad \text{(XIV)}$$

which gives $k_2 = 1.30 \times 10^{-5}$. As mentioned previously the concentrations of cupric chloride obtained in the electrolytic experiments were all less than that of the most dilute solution of Table IX. Accordingly the average of 1.30×10^{-5} and 1.11×10^{-5}, that is 1.2×10^{-5}, has been taken as the value of k_2 in the electrolytic experiments. Hence $l/k_2 = 333$.

The diffusion constant of cuprous chloride dissolved in hydrochloric acid may be calculated similarly from the value of $l/k_1 = 138$, and is found to be 2.9×10^{-5}. Although this value is noticeably higher than any that might be deduced from the mobility of $\overline{\mathrm{Cl}}$ or from the analogy of $\overline{\mathrm{CuCl_2}}$ with other complex ions, yet it seems unlikely that the value of k_1 can be less than 2.9×10^{-5} (that is, assuming $l = 4 \times 10^{-3}$) for in that case it would be necessary to assume that the solution at the immediate surface of the copper is supersaturated with respect to cuprous chloride.[1]

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[1] The mobility of Cu for binary electrolytes at infinite dilution is given by Kohlrausch and Holborn as 50. By analogy with Zn the value of the mobility of Cu in $CuCl_2$ may be taken as about 50.5.

DISCUSSION OF RESULTS

Table X gives, together with the experimental data, the values of K calculated according to equation IX. The numbers so found vary between 0.5×10^4 and 3.5×10^4. Bodländer and Storbeck's work in which copper powder and cuprous chloride were shaken with solutions of potassium chloride gives $K = 1.5 \times 10^4$. Considering the wholly different nature of the two series of experiments this agreement must be regarded as a remarkable confirmation of the theory of the electrolysis set forth in the introduction.

As, however, the values of K calculated according to equation IX, are largely and unequally affected by the unavoidable error of experiment, I have thought that a recalculation of the anode losses, assuming the constant $K = 1.5 \times 10^4$ would furnish a more satisfactory test of the validity of the theory.

In making this recalculation, $K = 1.5 \times 10^4$; $l/k_1 = 1.38$ and $l/k_2 = 3.33$ were substituted in equation IX, which then becomes,

$$\frac{\frac{(2Q-P)}{63.6}\left(\frac{1}{V}+\frac{3.33}{At}10^5\right)}{\left[\frac{2y(P-Q)}{63.6}\left(\frac{1}{V}+\frac{1.38}{At}10^5\right)\right]^2} = 1.5 \times 10^{-4}. \qquad \text{(XVI)}$$

For each experiment the proper values of Q, t, A and V, were then introduced and a value of y taken from the graph on the assumption that $\{\overline{\mathrm{Cl}}\} = [\overline{\mathrm{Cl}}]$. The resulting quadratic equation in $(P - Q)$ was solved, giving the value of P entered under "*P calc.*" next to the observed values.

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[1] In some of the experiments of Table IV, the copper cylinder became covered with a white coating of cuprous chloride.

In most of the experiments the observed and calculated anode losses agree to within 3 to 4 milligrams, although the conditions were varied to quite a large extent. Thus, the concentration of hydrochloric acid was varied from 4.65×10^{-3} to 16.15×10^{-3} normal, the current from 0.013 to 0.051 ampere, the anode area from 18 to 47 cm,^{2} and the rate of circulation of the electrolyte from 0.242 to 2.361 cm^3 per second.

The greatest discrepancies between "*P calc.*" and "*P obs.*" are to be found in those experiments whose duration was rather long, *e. g.*, Nos. 28, 35, 38, 43 and 57. This was undoubtedly due to oxidation of cuprous salt by air, which in spite of all precautions, must have entered the cell. A similar reason is to be assigned for the high anode losses observed with small currents. From the table it is seen that the differences in concentration of the cupric and cuprous salts at the electrode and in solution were very considerable, so that the corrections for diffusion were in many cases the main items in the calculation of K. Consequently any errors in measuring A or V/t, or any slight variation in the rate of stirring during the experiment affected the calculated value of K considerably. The fact that for low values of $\overline{\mathrm{Cl}}$, the anode losses calculated are uniformly greater than those observed (see experiments 7, 8, 12–16) must be ascribed to an error in the determination of y, which is quite probable in view of the form which the graph for it assumes for values of $\overline{\mathrm{Cl}}$ less than 5.5×10^{-3} (see Fig. 2).

As a further test of the validity of the theory I have also performed four experiments (see Table XI) in which a solution, approximately 9.0×10^{-3} normal in hydrochloric acid and 0.171×10^{-3} molar in cupric chloride was used as elec-

TABLE X

Room temperature; 1600 revs. per minute

No.	$10^3 \times [Cl]$	I (Amp.)	P obs.	P calc.	Q	V	t	$10^4 \times V/t$
1	11.60	0.0505	0.0752	0.0802	0.0599	2.99	3600	8.31
2	8.22	0.0498	0.1422	0.1460	0.1110	3.28	7200	4.56
3	13.50	0.0470	0.1438	0.1528	0.1113	5.80	7200	8.06
4	8.22	0.0436	0.1173	0.1174	0.0900	2.58	6000	4.30
5	9.18	0.0385	0.0613	0.0631	0.0456	6.43	3600	17.86
6	8.75	0.0250	0.0778	0.0850	0.0576	9.84	7200	13.68
7	5.29	0.0231	0.0402	0.0430	0.0297	2.53	3600	7.03
8	5.55	0.0253	0.0406	0.0439	0.0299	2.54	3600	7.05
9	12.60	0.0454	0.1469	0.1464	0.1080	3.45	7200	4.79
10	6.61	0.0246	0.0391	0.0404	0.0489	6.20	3600	17.22
11	4.65	0.0249	0.0691	0.0645	0.0502	2.32	6120	3.78
12	5.30	0.0250	0.1223	0.1278	0.0888	7.22	10800	6.68
13	5.27	0.0246	0.0407	0.0426	0.0293	2.47	3600	6.86
14	5.27	0.0246	0.0608	0.0635	0.0438	3.65	5400	6.75
15	5.24	0.0190	0.0800	0.0853	0.0570	6.20	9000	6.89
16	5.54	0.0246	0.0619	0.0630	0.0437	3.78	5400	7.00
17	9.14	0.0243	0.0410	0.0420	0.0288	6.70	3600	18.61
18	8.38	0.0252	0.0644	0.0641	0.0445	3.36	5400	6.22
19	8.05	0.0249	0.1106	0.1025	0.0738	2.18	9000	2.42
20	10.50	0.0450	0.0742	0.0761	0.0513	8.50	3600	23.61
21	8.65	0.0250	0.0863	0.0861	0.0593	4.87	7200	6.76
22	9.47	0.0300	0.1332	0.1340	0.0922	4.60	9000	5.11
23	5.22	0.0134	0.0694	0.0735	0.0476	7.15	10800	6.62
24	8.24	0.0247	0.0888	0.0865	0.0606	3.25	7440	4.36
25	9.34	0.0246	0.0644	0.0644	0.0437	9.57	5400	17.72
26	10.00	0.0225	0.1940	0.1900	0.1320	4.43	18000	2.46
27	5.48	0.0250	0.0656	0.0651	0.0442	3.63	5400	6.72
28	10.00	0.0430	0.4370	0.3980	0.2934	5.20	22600	2.41
29	16.15	0.0452	0.0810	0.0775	0.0536	2.80	3900	7.18
30	9.20	0.0229	0.0411	0.0400	0.0272	6.86	3600	19.05
31	9.21	0.0250	0.0742	0.0752	0.0491	4.10	6000	6.84
32	7.97	0.0248	0.0669	0.0620	0.0440	1.87	5400	3.46
33	6.05	0.0253	0.0683	0.0672	0.0450	3.48	5400	6.45
34	11.93	0.0240	0.0727	0.0710	0.0477	10.53	6000	17.55
35	8.20	0.0243	0.1530	0.1420	0.1006	4.30	12600	3.41
36	9.15	0.0251	0.0950	0.0973	0.0620	5.15	7500	6.87
37	9.26	0.0136	0.0310	0.0321	0.0202	7.84	4500	17.50
38	8.96	0.0350	0.1964	0.1830	0.1288	4.71	11700	4.02
39	9.00	0.0253	0.0924	0.0924	0.0601	5.80	7200	8.05
40	9.45	0.0400	0.1942	0.1800	0.1260	5.45	9000	6.06
41	7.90	0.0241	0.0880	0.0805	0.0575	2.30	7200	3.19
42	8.80	0.0194	0.0710	0.0703	0.0460	5.14	7200	7.14
43	8.96	0.0290	0.1840	0.1740	0.1200	5.45	12600	4.33
44	9.85	0.0420	0.1860	0.1740	0.1210	7.90	9000	8.79
45	10.00	0.0450	0.0782	0.0740	0.0505	3.60	3600	10.00
46	11.80	0.0236	0.0879	0.0828	0.0560	6.29	7260	8.66
47	9.37	0.0301	0.0837	0.0804	0.0535	3.89	5400	7.19
48	9.26	0.0133	0.0434	0.0430	0.0275	10.30	6300	16.35
49	8.45	0.0247	0.0924	0.0863	0.0585	2.95	7200	4.10
50	6.04	0.0252	0.0483	0.0440	0.0299	2.40	3600	6.66
51	8.95	0.0144	0.0548	0.0555	0.0341	5.30	7200	7.36
52	8.99	0.0194	0.0746	0.0720	0.0464	4.50	7200	6.25
53	12.00	0.0234	0.0904	0.0802	0.0558	3.05	7200	4.24
54	9.75	0.0200	0.0789	0.0749	0.0474	4.95	7200	6.12
55	9.31	0.0247	0.0967	0.0921	0.0585	4.80	7230	6.64
56	11.98	0.0140	0.0498	0.0477	0.0291	10.97	6300	17.42
57	8.46	0.0180	0.1397	0.1266	0.0824	7.60	14400	5.28
58	11.77	0.0137	0.0706	0.0636	0.0405	7.85	9000	8.73

TABLE X—(*Continued*)

No.	A	Percent Cuprous	$10^3 \times$ [Cupric]	$10^3 \times$ {Cupric}	$10^3 \times$ {Cuprous}	$10^3 \times$ **Cu {prous}**	$10^3 \times$ {Cl}	*Y*	$10^{-4} \times$ K
1	15.0	25.5	0.235	3.84	0.161	0.95	11.08	0.294	3.1
2	18.0	28.0	0.383	4.26	0.300	1.34	7.35	0.326	1.9
3	18.0	29.2	0.214	3.40	0.176	1.23	12.47	0.283	2.6
4	18.0	30.3	0.382	3.42	0.322	1.42	7.24	0.328	1.5
5	18.0	31.5	0.073	2.42	0.077	1.13	8.14	0.320	1.8
6	23.5	34.2	0.060	1.22	0.064	0.58	8.20	0.319	3.4
7	47.0	35.2	0.119	0.71	0.130	0.40	5.07	0.485	1.9
8	47.0	35.4	0.119	0.71	0.132	0.40	5.31	0.376	3.0
9	18.0	36.5	0.315	3.11	0.355	1.66	11.05	0.295	1.3
10	18.0	37.2	0.047	1.56	0.052	0.92	5.97	0.348	2.4
11	47.0	37.7	0.212	0.78	0.252	0.74	4.54	0.615	0.8
12	47.0	37.7	0.120	0.69	0.146	0.43	5.05	0.490	1.5
13	47.0	38.7	0.113	0.66	0.146	0.44	5.01	0.500	1.4
14	47.0	39.0	0.115	0.66	0.146	0.44	5.02	0.500	1.4
15	47.0	40.6	0.086	0.40	0.117	0.35	5.10	0.475	1.4
16	47.0	42.0	0.106	0.63	0.152	0.46	5.21	0.400	1.8
17	18.0	42.0	0.039	1.39	0.057	0.89	8.28	0.319	1.7
18	23.5	43.2	0.117	1.16	0.186	0.87	7.65	0.323	1.5
19	23.5	43.6	0.267	1.18	0.531	1.28	7.21	0.328	0.7
20	35.2	45.0	0.053	1.23	0.085	0.35	9.63	0.308	1.8
21	23.5	45.5	0.104	1.10	0.174	0.87	7.90	0.320	1.4
22	37.5	46.0	0.175	0.97	0.280	0.81	8.90	0.313	0.7
23	47.0	46.0	0.057	0.32	0.096	0.28	5.05	0.490	1.7
24	23.5	46.5	0.157	1.13	0.273	0.97	7.48	0.325	1.1
25	18.0	47.3	0.038	1.28	0.068	0.99	8.31	0.318	1.3
26	35.2	48.0	0.025	0.82	0.440	0.85	9.52	0.309	1.2
27	47.0	48.0	0.099	0.57	0.185	0.55	5.18	0.425	1.1
28	35.2	49.0	0.453	1.49	0.433	0.83	9.07	0.311	2.2
29	18.0	51.1	0.147	2.10	0.306	2.00	13.94	0.274	0.7
30	18.0	51.1	0.031	1.11	0.064	0.99	8.14	0.320	1.1
31	47.0	51.2	0.092	0.54	0.192	0.58	8.77	0.315	1.8
32	23.5	52.0	0.268	1.05	0.377	1.14	7.09	0.329	0.8
33	47.0	52.0	0.098	0.55	0.210	0.61	5.62	0.360	1.1
34	18.0	52.3	0.034	1.18	0.075	1.08	10.72	0.299	1.1
35	23.5	52.5	0.175	1.02	0.384	1.15	7.33	0.327	0.8
36	47.0	53.0	0.089	0.52	0.201	0.61	8.68	0.315	1.4
37	18.0	53.5	0.019	0.63	0.043	0.62	8.57	0.315	1.6
38	37.5	53.6	0.204	0.94	0.451	1.12	8.12	0.319	0.7
39	47.0	53.8	0.075	0.51	0.175	0.59	8.53	0.316	1.5
40	35.2	54.0	0.167	1.12	0.393	1.31	8.36	0.318	0.7
41	23.5	54.0	0.184	1.02	0.417	1.20	7.01	0.330	0.7
42	47.0	54.4	0.064	0.39	0.153	0.47	8.43	0.317	1.7
43	37.5	54.5	0.162	0.78	0.370	0.95	8.30	0.317	0.9
44	30.5	55.0	0.111	1.13	0.259	1.29	8.64	0.314	0.7
45	35.2	55.4	0.099	1.03	0.242	1.17	8.88	0.313	0.8
46	18.0	55.9	0.062	1.06	0.157	1.20	10.52	0.300	0.8
47	47.0	56.4	0.094	0.57	0.244	0.76	8.76	0.315	1.0
48	18.0	57.8	0.014	0.44	0.049	0.66	8.54	0.316	1.0
49	47.0	58.0	0.131	0.51	0.360	0.79	7.94	0.320	0.8
50	47.0	61.3	0.075	0.43	0.241	0.71	5.51	0.366	0.7
51	47.0	61.4	0.040	0.25	0.123	0.39	8.63	0.316	1.6
52	47.0	62.2	0.161	0.87	0.203	0.56	8.55	0.316	2.7
53	18.0	62.5	0.109	0.96	0.357	1.51	10.55	0.299	[illegible]
54	47.0	62.8	0.049	0.26	0.195	0.55	9.25	0.310	0.9
55	47.0	64.7	0.067	0.38	0.250	0.74	8.71	0.315	0.7
56	18.0	71.1	0.012	0.40	0.059	0.85	10.96	0.295	0.6
57	30.5	71.2	0.052	0.35	0.119	0.40	7.76	0.321	2.1
58	18.0	74.3	0.021	0.29	0.076	0.58	10.72	0.299	1.0

trolyte. In these experiments equation IX assumes the form:

$$\frac{\{\overset{++}{\mathrm{Cu}}\}}{\{\overset{+}{\mathrm{Cu}}\}^2} = \frac{\frac{(2\mathrm{Q}-\mathrm{P})}{63.6}\left(\frac{1}{\mathrm{V}}+\frac{10^3 l}{k_2\mathrm{A}t}\right)+0.171\times 10^{-3}}{\left[\frac{2\mathrm{Y}(\mathrm{P}-\mathrm{Q})}{63.6}\left(\frac{1}{\mathrm{V}}+\frac{10^3 l}{k_1\mathrm{A}t}\right)\right]^2}. \quad (\mathrm{IX}a)$$

In the Introduction the qualitative effect of changes in rate of stirring was discussed. Table XII gives the data for three electrolyses which were carried out with lower rates of stirring than that used in the other experiments. Under R is given the rate of stirring in revolutions per minute, and in the last column of the table, under C, is given the number of an experiment in Table X in which all the other variables were the same and which may thus be used for comparison. These experiments show that in accordance with the requirements of the theory the proportion of cuprous salt formed is less when the rate of stirring is decreased.

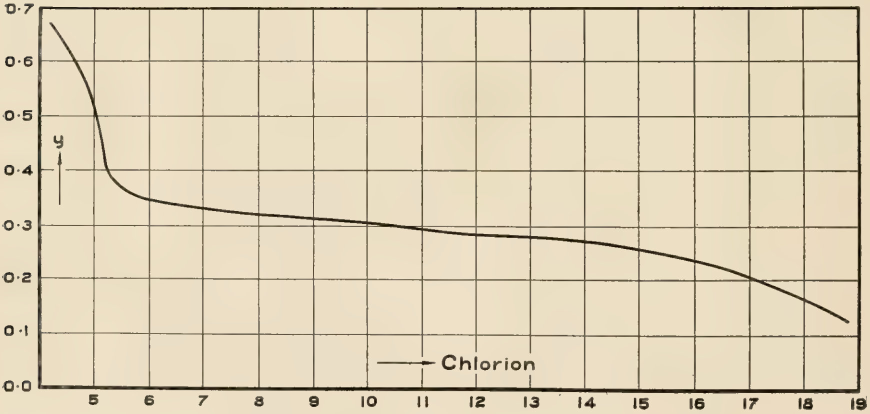

Fig. 2

TABLE XI

Concentration of $\overset{++}{Cu}$ in stock solution, 0.171 × 10^{-3} mols per liter.
Area of electrode = 23.5 cm^2. *R* = 1600. Room temp.

No.	$10^3 \times$ [Cl]	I (Amp.)	P obs.	Q	V	*t*	$10^4 \times V/t$	Per-cent Cu-prous
1	9.31	0.025	0.0990	0.0590	5.55	7200	7.64	67.7
2	9.31	0.025	0.0448	0.0290	5.23	3600	14.50	54.5
3	9.16	0.018	0.0728	0.0443	5.20	7200	7.23	64.3
4	9.20	0.018	0.0739	0.0450	5.65	7200	7.89	64.3

No.	$10^3 \times$ [Cupric]	$10^3 \times$ {Cupric}	$10^3 \times$ [Cuprous]	$10^3 \times$ {Cuprous}	$10^3 \times \{\bar{Cl}\}$	*Y*	$10^{-4} \times K$
1	0.396	2.83	0.229	1.253	8.05	0.320	0.6
2	0.382	4.73	0.095	0.288	8.34	0.318	1.2
3	0.219	0.71	0.172	1.138	8.27	0.319	0.6
4	0.216	0.71	0.169	0.904	8.30	0.319	0.9

TABLE XII

Area of electrode = 18 cms^2. Room temp.

R	$10^3 \times$ [Cl]	I (Amp.)	P	Q	V	*t*	$10^4 \times V/t$	Percent Cuprous	C
800	16.3	0.047	0.0896	0.0858	3.7	5400	6.86	4.3	29
1100	15.8	0.053	0.0681	0.0638	2.7	3600	7.50	7.0	29
1100	12.0	0.024	0.0804	0.0560	2.83	7200	3.92	43.5	53

In conclusion, I desire to express my thanks to Professor W. Lash Miller under whose direction the above investigation was carried out, for many valuable suggestions and kind encouragement during its progress.

SUMMARY

Having found that it was possible to make copper dissolve anodically in hydrochloric acid wholly as cupric or wholly as cuprous or as a mixture of these in any desired proportions depending upon the concentration of acid, current density, rate of stirring and rate of circulation of the electrolyte, it suggested itself that there may be equilibrium

at the surface of the anode between metallic copper and the cupric and cuprous salts in solution according to the equation,

$$\overset{++}{\mathrm{Cu}} + \overset{\circ}{\mathrm{Cu}} \rightleftarrows 2\overset{+}{\mathrm{Cu}}.$$

A number of experiments were therefore undertaken to test this supposition quantitatively.

As the concentrations of the cupric and cuprous salts at the electrode were very different from those in the solution—sometimes they were twenty times as great—they had to be calculated from the latter by allowing for diffusion.

In these calculations there was required a knowledge of l/k_1 and l/k_2 (where l denotes the thickness of the diffusion-film and k_1 and k_2 are the diffusion constants of cuprous and cupric salts respectively). A method was therefore devised for obtaining these constants experimentally.

Electrolyses were carried out in which the concentration of hydrochloric acid was varied from 4.65×10^{-3} to 16.15×10^{-3} normal, the current from 0.013 to 0.051 ampere, the anode area from 18 to 47 cms^2, and the rate of circulation of the electrolyte through the cell varied from 0.242 to 2.361 cm^3 per second. It was found that the fraction of copper dissolved as cuprous varied from 25 to 74 per cent.

From the values of the concentrations at the electrode as calculated for all these experiments, values of the "constant" $K = \{\overset{++}{\mathrm{Cu}}\}/\{\overset{+}{\mathrm{Cu}}\}^2$ were determined. These were found to be in good agreement with the number deduced from the equilibrium experiments of Bodländer and Storbeck in which copper powder and cuprous chloride were shaken with solutions of potassium chloride.

Finally, the fraction of copper dissolved as cuprous salt at a rotating anode in hydrochloric acid, with varying conditions of concentration of acid, current density, rate of rotation and rate of circulation of the electrolyte, was calculated from this theory and found to be in good accord with the experimental results.

Electrochemical Laboratory,
Toronto University.

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ERRATUM

P. 905. The headings of columns 6 and 7, Table X should read: 10 [Cuprous], and $10^3 \cdot$ [Cuprous] respectively.

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